U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-299 152

Antimony Removal Technology for Mining Industry Wastewaters

Hittman Associates, Inc, Columbia, MD

Prepared for

Industrial Environmental Research Lab -Cincinnati, OH

May 79

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-129	2.
3. RECIPIENT'S ACCESSION NO. PB299152	
4. TITLE AND SUBTITLE Antimony Removal Technology for Mining Industry Wastewaters	5. REPORT DATE May 1979 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C. Leon Parker, Efim Livshits, and Kathleen McKeon	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Hittman Associates, Inc. 9190 Red Branch Road Columbia, Maryland 21045	10. PROGRAM ELEMENT NO. 1NE623B
	11. CONTRACT/GRANT NO. 68-03-2566
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Lab. Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final 3/15/78 - 7/15/78
	14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report assessed the current state-of-the-art of antimony removal technology for mining industry wastewaters. Through literature review and personal interviews, it was found that most mines and mills reporting significant quantities of antimony in their raw wastewater had approximately 0.1 to 0.2 mg/1 antimony remaining after tailings pond settling. This reduction in antimony content without any chemical treatement indicates that for most mines and mills the antimony-containing wastewater components are in the form of suspended solids and may be easily removed.

Sulfide precipitation technology cannot remove soluble antimony to levels below 2.0 to 3.0 mg/1 and lime precipitation cannot lower levels below 1.0 mg/1. A minimum desired level of 0.5 mg/1 of antimony was selected for this technology assessment based on the effluent limitation recommended by the EPA BPCTCA in antimony mines. There is currently no demonstrated technology for achieving this minimum desired antimony level. Ion exchange and insoluble starch xanthate appear to be promising technologies for antimony removal; carbon adsorption, sodium borohydride reduction, and peat moss adsorption do not appear feasible.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Antimony inorganic compounds Tailings Beneficiation Neutralizing	Lime neutralization Ion exchange Insoluble starch xanthate Peat moss Carbon adsorption Drainage, mines	13B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 73
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PCA04 MFA01

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1979-657-060/5342

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/7-79-129
May 1979

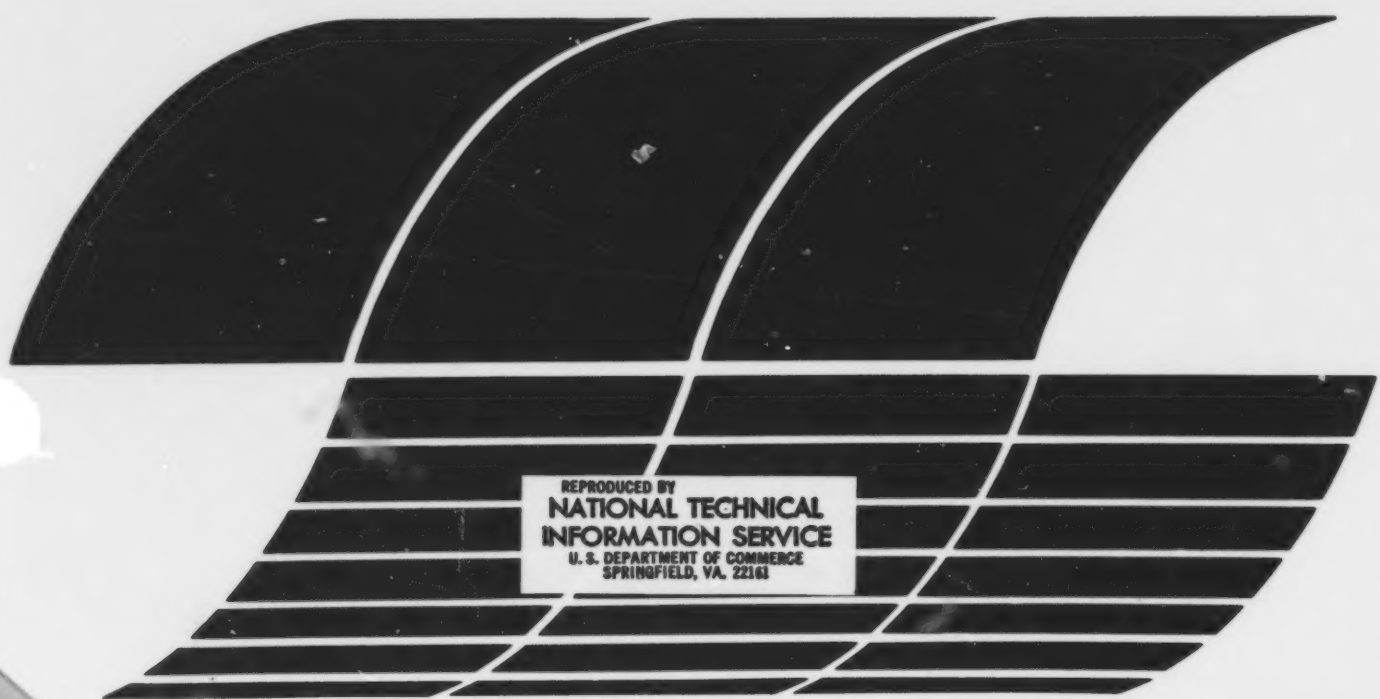
Research and Development

PB 299152

EPA

Antimony Removal Technology for Mining Industry Wastewaters

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/7-79-129
May 1979

ANTIMONY REMOVAL TECHNOLOGY FOR MINING INDUSTRY WASTEWATERS

by

C. Leon Parker
Efim Livshits
Kathleen McKeon
Hittman Associates, Inc.
Columbia, MD 21045

Contract No. 68-03-2566

Project Officer

Roger C. Wilmoth
Resource Extraction and Handling Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report reviews literature on treatment technology for removal of antimony from wastewaters in general and specifically from mining wastewaters. The results indicate that in many cases the antimony compounds are removed from mining wastes by simple sedimentation because they are either insoluble or adsorbed onto other insoluble materials. It appears the most promising treatment technologies for those cases requiring further antimony removal are starch xanthate and ion exchange. The information contained herein forms the basis for directing additional research and should be of interest to regulatory agencies, industry, and universities involved in environmental programs for mining industries. For further information on the subject, please contact the Resource Extraction and Handling Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This study was initiated with the overall objective of assessing existing antimony removal technologies and evaluating their potential for achieving minimum desired antimony levels in mining industry wastewaters. In the course of the assessment, both literature surveys and personal interviews were conducted.

During the course of the study it was found that most mines and mills reporting significant quantities of antimony in their raw wastewater had approximately 0.1 to 0.2 mg/l antimony remaining after tailings pond settling. This reduction in antimony content without any chemical treatment indicates that for most mines and mills the antimony-containing wastewater components are in the form of suspended solids and may be easily removed.

Information collected on antimony removal technologies useful for removing soluble antimony from the wastewater of the few mines and mills involved shows that sulfide precipitation technology cannot remove antimony to levels below 2.0 to 3.0 mg/l. Lime precipitation technology is not capable of removal to levels below approximately 1.0 mg/l. Neither of these commonly employed and recommended technologies, therefore, is suitable for achieving minimum desired antimony levels. A minimum desired level of 0.5 mg/l of antimony was selected for this technology assessment based on the effluent limitation recommended by the EPA BPCTCA in antimony mines. There is currently no demonstrated technology for achieving this minimum desired antimony level.

Application of cost and technical feasibility analysis to five potential antimony removal technologies (ion exchange, carbon adsorption, sodium borohydride reduction, peat moss adsorption, and insoluble starch xanthate treatment) indicates that ion exchange and insoluble starch xanthate treatment are the most promising candidates for further work. It is recommended that laboratory efforts be initiated to develop a demonstrated antimony removal technology not only for mine and mill wastewaters but also for smelters, battery manufacture, and other industries that have high antimony concentrations in their wastewater.

This report was submitted in fulfillment of Contract No. 68-03-2566 by Hittman Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This effort was performed in the period from March 15, 1978, to July 15, 1978.

CONTENTS

Foreword iii
Abstract iv
Tables viii
Acknowledgments ix

1. Introduction 1
2. Conclusions 2
3. Recommendations 4
4. Effluent Characteristics 5
   - Antimony occurrence in wastewaters 5
   - Reported data 5
   - Wastewater treatment. 14
5. Antimony Removal Technologies 18
   - Antimony chemistry 18
   - Sulfide precipitation 19
   - Lime precipitation. 20
   - Ion exchange 21
   - Starch xanthate 24
   - Activated carbon. 26
   - Peat moss 30
   - Sodium borohydride 31
6. Cost and Feasibility Analysis 36
   - Summary 36
   - Influencing parameters 37
   - Feasibility methodologies 42
   - Technology analyses 45

References 57

Preceding page blank

TABLES

Number		Page
1	Chemical Composition of Raw Wastewater Discharged from Antimony Flotation Mill	7
2	Antimony Leach Plant Effluent and Tailings Pond Effluent at the Sunshine Mine, 1975	8
3	Composition of Antimony-Containing Raw Wastewater from Three Mines and Mills	10
4	Antimony Concentrations in Wastewaters from Primary and Secondary Nonferrous Smelting (Exluding Secondary Lead)	11
5	Raw Waste Characteristics - Secondary Lead Smelters	12
6	Typical Effluent Analysis of a Paint Plant	13
7	Metallic Pollutants in a Dye House Wastewater Stream Before and After Pilot Plant Peat Moss Treatment	13
8	Suspended Solids and Total Antimony Removal by Mine Tailings Pond	14
9	Monthly Average and Maximum Effluent Concentrations (1975) Lime Treatment System, Secondary Lead Plant 4131	16
10	Performance of Lime Treatment at Secondary Lead Plant 4131	17
11	Activated Carbon Adsorption of Selective Metals	28
12	Percent Removal with Removal Technology Combinations	29
13	Treatment of Wastewaters Containing Heavy Metals	32
14	Summary of Process Applicability Estimates for Antimony Removal	55

ACKNOWLEDGMENTS

The cooperation and assistance of Mr. Roger Wilmoth, EPA Project Officer, and numerous individuals in EPA Regions 1, 6, 7, 8, 9, and 10 offices in arranging for contacts, visits, and information collection with various mines is gratefully acknowledged, as is the assistance provided by the California Regional Quality Control Board and the Nevada State Environmental Commission. Gratitude is also expressed for the assistance provided by Mr. M. Jarrett, Mr. R. Kirby and Ms. P. Williams of EPA Effluent Guidelines Division, Washington, D.C.

Mining company representatives who not only supplied pertinent information but also were kind enough to devote additional time during mine visits are listed below:

Mr. Emil Fattu
Sunshine Mining Company
Kellogg, Idaho

Mr. Walt Wide
Hecla Mining Company
Wallace, Idaho

Mr. George Lawrence
U.S. Antimony Corporation
Thompson Falls, Montana

Mr. Victor Botts
Placer Amax
McDermitt, Nevada

Mr. George Brewer
Union Carbide Corporation
Bishop, California

In addition to the assistance provided in collecting mine information, various individuals also contributed significant information regarding treatment technologies. These individuals included:

- Mr. J. Dick, ICI Product Division, Wilmington, Delaware
- Mr. John Zschiegner - J&J Materials, Neptune City, New Jersey
- Mr. Allan Bessimer, Allan Bessimer Extract Systems, Manasquan, New Jersey
- Mr. K. Jones, Mining Chemicals Group, Dow Chemical Co., Midland, Michigan

- Mr. John Bell, Mogul Corporation, Chagrin Falls, Ohio
- Mr. Michael Cook, Ventron Corporation, Beverly, Massachusetts
- Mr. R. Wing, U.S. Department of Agriculture, Northern Regional Research Laboratory, Peoria, Illinois

SECTION 1

INTRODUCTION

Antimony and its compounds have been designated by EPA as toxic substances. Significant concentrations of antimony have been observed in many discharges from the mining industry, particularly the beneficiating processes. Current technology involves antimony removal by lime precipitation; however, this technique was questioned as to its ability to reduce the antimony concentration to desired levels of less than 0.5 mg/l.

The purpose of this study was to assess existing antimony removal technologies and to evaluate the potentials of these technologies for achieving minimum desired antimony levels. A minimum desired level of 0.5 mg/l of antimony was selected for this technology assessment based on the effluent limitations recommended by EPA BPCTCA in antimony mines (1). The study entailed data collection on the chemistry and solubility of antimony compounds and on reported treatment technologies and their performance through published literature review and personal communications with the mining industry, researchers, chemical suppliers, and wastewater treatment equipment manufacturers.

In order to assess and evaluate the antimony removal technologies, a methodology was developed to rate the various technologies as to probability of successful technical application, cost impact, and overall feasibility. The probability of successful technical application was determined from the combined products of probability ratings for: (1) theoretical achievement of the desired antimony removal level, (2) availability of materials and equipment, (3) interference effects, and (4) estimated ability of research and development efforts to overcome existing problems. Cost impacts were estimated as a percentage of annual product(s) value. The overall feasibility ratings were determined by dividing the probability of successful technical application by the cost impact value. The results of these ratings provide direction for future research efforts.

SECTION 2

CONCLUSIONS

As a result of this study, a number of conclusions were reached that relate to antimony removal technology and its performance as applied to mining industry wastewater. Most of the mines and beneficiating mills which have measured antimony in their raw effluent discharge wastewaters report values that are significantly below 1 mg/l antimony content, even though the raw wastewater prior to tailings pond settling often have much higher values. This dramatic decrease in antimony content with no treatment other than a settling pond indicates either that much of the reported total antimony is in the form of settleable solids or that antimony is adsorbed onto these solids and co-precipitates with them.

For tne few mines where antimony is present in amounts greater than 0.1 to 0.2 mg/l in the discharged wastewater, no known demonstrated removal technology for reducing it to these levels has been found. In fact, very little work has been reported on antimony removal below 0.5 mg/l for any technology, even at the laboratory level.

Lime precipitation removes antimony from wastewater to the approximate level of 1 mg/l. In some cases, even lower values have been reported, but these values are rarely below 0.5 to 0.7 mg/l. Sulfide precipitation which yields solubility values of approximately 2 mg/l and reported laboratory results of 3.5 mg/l may not be a practical technology for antimony removal to the desired level of less than 0.5 mg/l. Lime precipitation gives significantly lower residual antimony contents than these reported sulfide precipitations.

Two other treatment technology areas not covered extensively in this report are plant-specific technologies and technologies which are primarily geared toward water recovery. Plant-specific technologies include zero discharge, recycle, reuse, and solar evaporation options which may be applicable for specific locations and circumstances, but are not generally usable. Technologies which have water recovery

as their primary purpose include distillation, freeze drying, reverse osmosis, and electrodialysis. These technologies recover water but usually leave a concentrated solution which requires further treatment or disposal.

In order to achieve antimony removals from mining industry wastewaters to levels below 0.5 mg/l, new treatment technology needs to be developed and demonstrated. Results of the cost and feasibility analysis of Section 6 of this report indicate that ion exchange or insoluble starch xanthate treatment technologies are the most likely candidates to achieve the desired antimony removal.

In order to keep ion-exchange and insoluble starch xanthate removal technologies in perspective, however, it should be emphasized that:

- As removal technologies for antimony, both ion exchange and insoluble starch xanthate are still in the research laboratory stage, and only a small amount of work has been done at this level.

- Down to a level of approximately 1.0 mg/l residual antimony concentration, lime precipitation has been widely demonstrated to be the most practical and economical antimony removal technology.

- Both ion exchange and insoluble starch xanthate antimony removal technologies should be considered as polishing operations to remove most of the last mg/l of antimony remaining after other treatment.

- Other antimony removal or control technologies such as zero discharge, recycle, water reuse, process stream segregation, and solar evaporation are often feasible in individual mining wastewater situations. These options should be explored prior to turning to the technologies evaluated in this report.

SECTION 3

RECOMMENDATIONS

Since antimony compounds are included on the EPA toxic substances and priority pollutants lists and there is no demonstrated technology for their removal below approximately 1 mg/l residual concentration from mining, smelting, battery production, paint, or other industrial wastewaters, it is recommended that efforts be initiated to develop such technology.

It is recommended that the technology development include the following steps:

- Soluble antimony-containing wastewaters which are representative of those in the mining, smelting, battery production, and other industries should be selected. The total number of selected samples should not be greater than six.

- Laboratory screening of the samples should be made to determine the chemical form and level of the antimony present and its removal characteristics for simple treatments such as lime and sulfide precipitations.

- Bench-scale screening experiments should be made on the selected samples, using the findings of the initial laboratory screening, to determine promising antimony removal technologies. Ion exchange, carbon adsorption, and insoluble starch xanthate experiments should be included.

- There should be a pilot plant scale-up of the bench-scale results for one or more antimony-containing wastewater streams. The pilot plant could be located at an actual mine or other industrial site.

- A full-scale treatment unit should be installed and demonstrated.

SECTION 4

EFFLUENT CHARACTERISTICS

ANTIMONY OCCURRENCE IN WASTEWATERS

Antimony is present in wastewaters of the metals mining, primary and secondary nonferrous metals smelting, and paint and surface coating manufacturing industries. It is found in the effluents of dye houses, and in the coal-ash basins of power plants. It may also appear in the wastewaters from the manufacture of bearings, storage batteries, pewter, lead electrodes, and glass (1,2,3,4,5,6).

Over a hundred mineral ores containing antimony exist in nature. The most important is the antimony mineral stibnite (Sb_2S_3). This mineral is usually mined for primary antimony production. The most important ores from the standpoint of their wastewaters containing antimony are silver and lead ores from Idaho, Montana, and Nevada. The following minerals, used for the extraction of base metals, contain significant amounts of antimony: tetrahedrite (the sulfide of zinc, copper, and antimony), up to 29 percent antimony; jamesonite (the sulfide of lead and antimony), up to 35 percent antimony; and bournonite (the sulfide of copper, lead, and antimony), up to 25 percent antimony (1). Antimony is also associated with gold and mercury-bearing ores.

The following sections report the available data on antimony presence in the raw wastewater and treated effluents from the metal mining, smelting, and other industries mentioned above.

REPORTED DATA

Nonferrous Metals Mining and Milling

At present, the U.S. Antimony Corporation, whose Babbit Mine is in Thompson Falls, Montana, is the only domestic company mining and milling antimony as a primary product. The ore is extracted from an underground drift mine; there is no wastewater discharge from the mine. The adjacent antimony mill employs a froth flotation process to concentrate the antimony sulfide.

Water in this operation is added between the crushing and grinding stages at the rate of 305 to 382 cubic meters per day (3). Pollutants in the raw wastewater originate from the solubilization and dispersion of ore constituents and also from the introduction of the milling reagents. Table 1 shows the chemical composition of raw wastewater discharged from the antimony mill (3). This wastewater is directed to the retention ponds at the rate of 286 to 343 cubic meters per day. There is no discharge from the retention ponds (3). An analysis of the pond water gave the following results for the major heavy metals (3):

Total antimony	0.24 mg/l
Total arsenic	0.07 mg/l
Total zinc	0.09 mg/l

Tailings solids contain an average of 0.4 mg/l antimony in the form of Sb_2O_3, HSb_2O_5, and/or $Sb_2O_3 \cdot Sb_2O_5$ (Personal communication: Mr. John Lawrence, U.S. Antimony Corporation). Some stibnite (Sb_2S_3) may also be present in the solids. Dissolved antimony would be derived from the tailings, hence could be in either a trivalent or pentavalent state.

The Sunshine Mining Company, located in the Coeur d'Alene district of Idaho, recovers antimony by electrowinning from the NaOH leach of silver-copper ore. The effluents from the leach plant are directed to a tailings pond. The supernatant from the pond is discharged to the surface water (1975). Table 2 gives a comparison of the raw wastewater from the antimony leach plant and the effluent from the tailings pond. The tailings pond receives both wastewater from the leach plant and the tailings from the flotation process at the silver mill. The influent and effluent samples collected at the tailings pond during the period 1969 to 1971 showed mean influent, seepage, and effluent Sb concentrations to be 8.9, 79.8, and 33.3 mg/l, respectively (7). This strange distribution of antimony can be explained by the daily variation of antimony in the influent to the pond. Thus, the same study found antimony in the influent to the pond to be in concentrations above 60 mg/l in the morning hours and below 5 mg/l (which was the lower limit of detection) during the rest of the day (7).

In 1971 the Sunshine Mining Company effluents were reported to contain 5 to 40 mg/l of antimony (8). Plans, however, were underway to install a system for complete recycle of the antimony in the effluent from the electrolytic production of antimony back to the antimony plant influent (ore leach). Nevertheless, data from 1975 show the presence of significant amounts of antimony in the tailings

TABLE 1. CHEMICAL COMPOSITION OF RAW WASTEWATER DISCHARGED FROM ANTIMONY FLOTATION MILL (3)

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
pH	8.3*	Hg	0.0038
Acidity	8.5	Ni	0.10
Alkalinity	11.0	Tl	0.05
Color	113+	V	0.2
Turbidity (JTU)	170	K	3.5
TSS	149	Se	0.036
TDS	68	Ag	0.02
Hardness	40	Na	2.0
Chloride	1.5	Sr	0.11
COD	43	Te	0.2
TOC	7.8	Ti	0.5
Al	6.2	Zn	4.35
As	0.23	Sb	64.0
Be	0.002	Mo	0.2
Ba	0.3	Oil and grease	1
B	0.01	MBAS surfactants	1.9
Cd	0.103	Cyanide	0.01
Ca	0.57	Phenol	0.022
Cr	0.04	Fluoride	0.1
Cu	0.12	Total kjeldahl N	1.3
Total Fe	18.8	Sulfide	0.5
Pb	0.13	Sulfate	16.5
Mg	1.93	Nitrate	2.55
Total Mn	0.40	Phosphate	0.05

*Expressed in pH units.

+Expressed in cobalt units.

TABLE 2. ANTIMONY LEACH PLANT EFFLUENT AND TAILINGS POND EFFLUENT AT THE SUNSHINE MINE, 1975 (8)

Major wastewater parameter	Leach plant effluent (mg/l)	Tailings pond effluent (mg/l)
pH	13.2*	8.0*
Total solids	355,000	496
Suspended solids	355,000	20
Dissolved solids	128	476
Acidity		14
Alkalinity		45
Hardness		137
Chlorides		2
COD	1,500	51.5
TOC	7,000	12
SO_4		368
Oil & grease		10
Sulfide	430	0.5
As		0.73
Cd	1.3	0.02
Ca		19.5
Cu	0.22	0.02
Pb	0.25	0.1
Mg		13.5
Hg	0.0222	0.0023
Mn	0.02	1.3
Te	25	0.3
Zn	0.02	0.02
Sb	24	4.4
Mo	5.72	0.66

*Expressed in pH units.

pond effluent. The flow rate of discharge from the tailings pond in 1975 was 3.4 m^3/min.

A recent visit was made to the Sunshine Mining Company to discuss present levels of antimony in the leach plant bleed stream and tailings pond effluent. Total antimony levels were found to be higher in the leach plant bleed stream than shown in the 1975 data, namely 75 mg/l in March and 160 mg/l in May of 1978. Total antimony levels, however, for tailings pond effluents did not exceed 0.8/mg/l for both of these months (Personal communication: Mr. Emil Fattu, Sunshine Mining Company). Possible forms of soluble antimony from the leach plant bleed stream include Na_3SbS_3, Na_3SbS_4, and $H_4O_7Sb_2.H_2O\cdot 2Na$, with the final two forms being most probable (Personal communication: Fattu). Thus, pentavalent antimony is the most probable dissolved form.

During the survey of seven mines in the Coeur d'Alene district (1969 to 1971), antimony was found only at the Sunshine Mine (7). The limit of detection, however, for this particular study was 5 mg/l. In 1975 (3) and 1977 (8) antimony was found in the raw wastewater of ferroalloy, silver, and mercury mines and mills. Table 3 summarizes available data for these mines. The flow rates of the raw wastewater for these mines were: Mine 6101, 10,170 m^3/day; Mine 4401, 3,680 m^3/day, and Mine 9202, 5,390 mg/day (9).

Primary and Secondary Smelting of Nonferrous Metals

Antimony presence in lead, copper, zinc, and other metal concentrates ranges from insignificant to several percent. Because of the ubiquity of antimony, it may be found in a wide range of concentrations in the wastewaters from smelting operations. Table 4 presents available data on antimony in wastewaters from primary and secondary nonferrous smelting, excluding secondary lead. Secondary lead smelting is a source of secondary antimony. Antimony is persistently present in significant concentrations in the wastewater from the secondary lead plants. Table 5 gives the chemical composition of wastewater streams from six secondary lead plants. The plant numbers in the table are given as they appear in the EPA Development Document for Effluent Limitation Guidelines for Miscellaneous Nonferrous Metals (10).

Other Industries

Antimony and its compounds are widely used in the production of paints and in the dye houses of the textile

TABLE 3. COMPOSITION OF ANTIMONY-CONTAINING RAW WASTEWATER FROM THREE MINES AND MILLS (3)

	Mine No.* 6101	Mine No.* 4401	Mine No.* 9202
Mine and mill description	Molybdenum	Copper	Mercury
Wastewater stream	Tailings pipe effluent	Influent to tailings pond	Influent to tailings pond
Wastewater parameter	(mg/l)	(mg/l)	(mg/l)
pH (units)		7.4	8
Total suspended solids	10	397,000	139,000
Volatile suspended solids		62,800	4,300
COD	10	15,100	60
TOC	5	25	1
Sb	1.3	18	53
As	0.01	0.8	1.1
Be		0.02	0.09
Cd		0.01	0.56
Cr		0.38	0.46
Cu	51	15	0.85
Pb	2.3	27	1.0
Hg		0.007	230
Ni		0.39	1.6
Se		0.04	0.01
Ag		2.2	0.01
Th		0.1	76
Zn	13.5	4.6	2.4
Phenol		0.01	76
Bis/2-ethylhexyl phthalate		15	9.2
Di-n-butyl phthalate		27	56
Diethyl phthalate		51	66
2,4-dimethylphenol			140

*Mine numbers are taken from Reference 3.

TABLE 4. ANTIMONY CONCENTRATIONS IN WASTEWATERS FROM PRIMARY AND SECONDARY NONFERROUS SMELTING (EXCLUDING SECONDARY LEAD) (10)

Smelter	Secondary copper plant 1					Secondary copper plant 2
Wastewater stream no.	1	2	3	4	5	1
Antimony concentration (mg/l)	8	135	20	1	3	2

Smelter	Columbium/tantalum Plant 1			Plant 2			Secondary silver		
Wastewater stream no.	1	2	3	1	2	3	1	2	3
Antimony (mg/l)	2.9	4.5	0.2	20	4	30	12	.7	1.5

TABLE 5. RAW WASTE CHARACTERISTICS - SECONDARY LEAD SMELTERS (10)

Type of Waste	Plant No.	Water analysis (mg/l, except pH)												
		pH	TSS	TDS	Pb	Sb	Cd	As	Zn	Cu	Fe	SO_4	Oil and Grease	NH_3
Battery acid	4131	<1.0	444	37,800	283	31.9	4.92	0.850	1.72	1.23	-	27,000	-	-
	4132	<1.0	1,390	-	37.1	23.8	0.075	4.6	1.09	3.15	16.4	123,000	-	-
	4133	<1.0	382	-	115	60.0	1.022	1.6	2.58	2.46	96.0	87,500	-	-
	4133 (case wash-water)	1.15	258	10,400	146	8.3	0.120	0.4	0.410	0.484	114.0	6,250	-	-
	4134	<1.0	1,050	-	6.13	62.0	5.23	2.7	4.21	4.54	69.0	170,000	-	-
Scrubber water	4131 (SO_2 scrubber)	1.5	2,320	209,000	54	8.3	1.62	1.250	0.17	0.11	-	58,500	-	-
	4132 (reverbatory & blast furnace)	4.75	85	462	191	1.0	0.432	1.4	0.900	0.025	2.32	11	-	-
	4132 (refining kettle)	7.90	12	2,270	6.24	28.0	0.030	430	0.40	0.144	1.42	310	-	-
	4133 (refining kettle)	5.50	94	3,740	970	170	0.215	146	0.460	1.44	2.20	10	-	-
Influent to treatment plant	4131	1.3	134	10,200	76	8.5	0.83	0.024	0.53	0.41	-	6,600	-	-
	4132	1.25	1,320	1,160	677	43.0	0.345	1.8	1.13	1.21	19.1	10,500	-	11.0
	4133	<1.0	568	-	45.4	91.0	1.55	2.6	4.43	3.26	278	52,500	-	14.8
	4135	<1.0	1,390	-	71.6	210	7.54	5.5	245	20.9	403	90,000	236	17.5
Plant runoff	4131	4.55	10	3,720	1.85	0.4	0.048	0.053	1.13	0.18	-	1,200	-	-
	4134	6.35	248	898	164	5.9	0.872	0.2	1.97	0.23	4.84	330	-	-
Non-contact cooling water	4133	7.7	3	230	0.3	1.50	<0.005	<0.1	0.06	0.020	0.07	11	-	-
	4136				10.2	0.79	0.04	0.22	0.13	0.015	-	-	-	-

industry. Table 6 shows analysis of a typical effluent from a paint plant (6). Table 7 gives the chemical composition of a dye house effluent before and after treatment (pilot plant type). Antimony also appears in trace concentrations in the coal-ash basins from coal-fired power plants (5).

TABLE 6. TYPICAL EFFLUENT ANALYSIS OF A PAINT PLANT (6)

Typical for a complete spectrum of a paint plant (mg/1)		Latex paint manufacture (mg/1)	Alkyd resin manufacture (mg/1)
COD	6200	13,000	500
BOD	4200	8,000	300
pH	7-10	7-11	7
Suspended solids	700-2000		
Total solids		6,500	1,300
Chromium	0.2	0.02	0.1
Zinc	6	8	0.4
Lead		2	0.8
Antimony	5	3	2
Tin	10	15	3
Iron	20	3	2

TABLE 7. METALLIC POLLUTANTS IN A DYE HOUSE WASTEWATER STREAM BEFORE AND AFTER PILOT PLANT PEAT MOSS TREATMENT (4)

Metal	Before treatment (mg/1)	After treatment (mg/1)
Cyanide	UL	0
Fluoride	NA	NA
Aluminum	NA	NA
Barium	NA	NA
Cadmium	25	0.1
Chromium (+6)	300	0.04
Chromium (+3)	300	0.25
Copper	250	0.2
Iron	31.5	0.25
Lead	8.4	0.025
Manganese	NA	NA
Nickel	67.5	0.05
Silver	NA	0.05
Zinc	7.5	0.08
Antimony	30.0	0.50
Mercury	15.0	0.01

NA = Not available
UL = Unlimited

WASTEWATER TREATMENT

Nonferrous Metals Mining and Milling

Since mining and milling are usually adjacent operations, the wastewaters from both operations are usually combined and flow to one treatment system. Treatment usually consists simply of sedimentation; i.e., use of one or more tailings ponds to remove suspended solids and, in some cases, heavy metals. Depending on solids loading and settling characteristics, a flocculant may or may not be necessary. If needed, the flocculant is usually combined with the influent stream before it enters the pond.

Tailings ponds may or may not have a point-source discharge depending on availability of water, effluent characteristics, leakage, and evaporation-precipitation ratios. Mining and milling operations in arid regions usually combine zero discharge treatment with almost total water recycle.

Although no treatment system has been designed to specifically remove antimony, there is usually a net reduction in total antimony from the influent to the effluent of the tailings pond, suggesting that the antimony is largely suspended and/or is captured via co-precipitation with other flocculating materials.

Table 8 presents data on suspended solids and total antimony levels in tailings pond influents and effluents from selected mining and milling operations having significant levels of antimony in their raw wastewaters. It is apparent that the antimony removed is very much related to the removal of suspended solids.

TABLE 8. SUSPENDED SOLIDS AND TOTAL ANTIMONY REMOVAL BY MINE TAILINGS POND (8)

Mine type	Influent, mg/l		Effluent, mg/l		Removal efficiency (%)	
	SS	Total Sb	SS	Total Sb	SS	Total Sb
Silver/ lead	396,000	18	18	0.2	99.9+	98.5
Mercury	139,000	53	1.6	0.2	99.9+	99.6

*Zero discharge system, sample was taken from recycle sump.

The data suggest that some soluble antimony may be present which is not removed by the tailings pond. All available data indicate, however, that total antimony levels in effluents of non-zero discharge tailings ponds from known mine and milling operations are usually far less than 1 mg/l, excepting the Sunshine Mining Company effluent, which has been found to range from 0.59 to 1.64 mg/l total antimony in recent years (1975 and 1978) (11,12). Data from March and May of 1978 indicate that antimony levels in the Sunshine effluent have been averaging approximately 0.7 mg/l (11). Sunshine is an exception because of its antimony leaching operation, which has been found to contain as much as 160 mg/l total antimony in the bleed stream flowing to the tailings pond (Personal communication: Fattu).

Secondary Lead Smelting and Refining

Existing treatment processes employed in the industry consist of:

- Lime treatment
- Ammonia treatment (pH adjustment).

In lime treatment systems, quicklime (CaO) or hydrated lime ($Ca(OH)_2$) is used to neutralize acidity and to precipitate dissolved heavy metals. Contact with lime is followed by clarification or settling. Flocculants are often added to promote faster settling.

The typical amount of lime used to neutralize 83 m^3/day of wastewater was given as 1,000 kg of $Ca(OH)_2$/day. The concentration of antimony in the effluents from this lime treatment system was reported to be 1.3 mg/l. Tables 9 and 10 show respectively effluent concentrations and a comparison of influent and effluent characteristics for a secondary lead plant.

Treatment with ammonia is used in secondary lead smelting and refining primarily to neutralize waste battery acid prior to its discharge into sanitary sewers. Ammonia is not effective in the removal of antimony. The following is the reported data on antimony removal with the ammonia treatment system (10):

	Antimony, mg/l	
	Influent	Effluent
Case 1	43.0	1.5
Case 2	91.0	77.0
Case 3	210.0	47.0

TABLE 9. MONTHLY AVERAGE AND MAXIMUM EFFLUENT CONCENTRATIONS (1975) LIME TREATMENT SYSTEM, SECONDARY LEAD PLANT 4131, (10)

	Discharge levels (mg/l)																
	pH (units)			TSS		Pb		Sb		As		Cu		Zn		Ni	
Month	Minimum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Jan.	3.10	7.72	8.95	4,085	5,902	0.39	2.24	1.16	2.61	<0.004	0.037	0.033	0.134	0.103	0.305	0.004	0.18
Feb.	5.24	7.33	8.55	4,058	8,326	0.37	1.63	1.43	3.10	<0.004	0.015	0.038	0.093	0.258	0.670	0.132	0.60
March	6.88	7.57	8.29	4,313	8,776	0.57	1.43	1.33	2.30	<0.009	0.033	0.039	0.068	0.352	1.29	0.104	1.22
April	6.97	8.14	10.00	4,096	5,892	0.35	0.88	0.76	1.39	<0.007	0.027	0.032	0.067	0.112	0.51	0.051	0.14
May	3.10	7.54	9.60	4,009	5,120	0.36	2.30	0.69	1.43	<0.004	0.026	0.033	0.130	0.005	0.45	0.038	0.12
June	7.30	8.03	9.70	3,766	4,638	0.104	0.32	0.79	1.96	0.003	0.008	0.021	0.043	0.013	0.045	0.019	0.039
July																	
Aug.	7.04	8.31	10.20	3,904	5,686	<0.072	0.17	0.80	1.25	<0.002	0.002	0.020	0.034	0.033	0.061	0.015	0.061
Sept.	7.00	7.94	10.15	4,080	6,458	0.16	0.74	0.69	1.61	0.003	0.019	0.027	0.054	0.020	0.20	0.040	0.090
Oct.	2.60	7.93	9.35	4,498	6,078	0.228	2.65	0.83	1.64	0.003	0.007	0.033	0.22	0.050	.49	0.043	0.14
Nov.	5.55	8.12	9.13	4,442	7,398	0.155	0.81	1.09	2.18	0.004	0.027	0.025	0.073	0.020	0.13	0.052	0.30

TABLE 10. PERFORMANCE OF LIME TREATMENT AT SECONDARY LEAD PLANT 4131 (10)

Parameter	Influent, mg/l	Effluent, mg/l
TSS	134	24
TDS	10,200	5,120
pH	1.3*	8.85*
Pb	76	0.41
Sb	8.5	0.70
Zn	0.53	0.03
As	0.024	0.03
Cu	0.41	0.03
Cd	0.83	0.005
Fe		
SO_4	6,000	2,530

*Expressed in pH units.

SECTION 5

ANTIMONY REMOVAL TECHNOLOGIES

ANTIMONY CHEMISTRY

Antimony is a group five element commonly found in nature as antimony trisulfide (stibnite) or in lower-grade ores as antimony trioxide. It may exist in dilute solutions as Sb^{+3} or Sb^{+5} cations or more probably as the $SB(OH)_6^-$ anion or other anionic complexes in which SbO^+ is the nucleus (13,14,15).

In wastewaters from mines and smelters, the main antimony compounds of concern are antimony trioxide, antimony trisulfide, organic chelates of antimony, and hydrolyzed antimony complexes. Antimony trioxide and antimony trisulfide are soluble below 1.0 mg/l and 1.7 mg/l, respectively. Below these concentrations, hydrolysis of antimony becomes particularly significant. Little is known about the stability and formation of organic antimony chelates.

Stability constants for antimony complexes either are not readily available or differ widely from one data source to another. Formation constants of hydroxy complexes are remarkably large when compared with most other ligands (15). This explains why with most highly charged metal ions, such as antimony ions, hydroxides or hydrous oxides are the only thermodynamically stable forms, except for multidentate ligands (15). $H[Sb(OH)_6]$ is thought to be the stable form in most natural waters (1).

Antimony in dilute solution undergoes deep hydrolysis, leading to the formation of its colloidal basic salt containing SbO^+ or its hydroxide (13). As was postulated by Bronsted, multivalent ions participate in a series of consecutive proton transfers. Hydrolysis may go beyond the uncharged species to form anions such as $Sb(OH)_6^-$ (15)

Like all metals, antimony is in a continuous search for a partner to improve its stability. The coordinated water may be exchanged for a preferred ligand. Metals in this respect are Lewis acids, able to accept a pair of electrons. Metal ions have speciation which is dependent upon the

stability of the hydrolysis products and the tendency of the metal ion to form complexes with other ligands.

Literature on antimony removal technology, with the exception of that on lime precipitation, is sparse, scattered, and often contradictory. Researchers for this study were unable to find a mine that treats its wastewater for antimony. Very little laboratory work has been done on developing removal technology. Within this framework, antimony removal technologies for which some information exists are discussed in the following subsections.

SULFIDE PRECIPITATION

In most cases, the theoretical solubilities of heavy metal hydroxides are considerably higher than the solubilities of the sulfides. It is this property of heavy metal sulfides that makes sulfide precipitation attractive. The Sulfex process patented by Permutit is among the most attractive of the sulfide precipitation methods. In conventional sulfide precipitation it is nearly impossible to consistently add the exact amount of sulfide required. Excess quantities of the sulfide source liberate hydrogen sulfide. This problem is eliminated in the Sulfex process by adding another heavy metal sulfide whose solubility is too low to release hydrogen sulfide but high enough to react with heavy metals (16).

Two metal sulfides commonly used are iron sulfide (solubility = 3.4×10^{-5} mg/l) and manganese sulfide (2.1×10^{-3} mg/l) (16). For a significant number of heavy metals this process is very effective, since the concentration of free sulfide at equilibrium is many orders of magnitude greater for iron sulfide than it is for other heavy metals. The Sulfex process, however, would not be effective in reducing dissolved antimony to recommended levels of less than 0.5 mg/l, and sulfide treatment in general is not adequate to obtain the desired levels. The reasons why Sulfex and sulfide precipitation are not recommended are as follows:

- Antimony trisulfide has a solubility of 1.7 mg/l. Sulfide precipitation cannot be expected to remove antimony sulfide below that solubility, assuming equilibrium conditions. In treating an ethylene glycol wastewater containing antimony by sulfide precipitation, concentrations of less than 3.5 mg/l were not attainable. Details of this experiment are not available.

- Most heavy metals commonly found in mining wastewaters have solubility as sulfide lower than antimony and would precipitate first. Iron sulfide and magnesium sulfide could not be used to control hydrogen sulfide formation because they are less soluble than antimony sulfide. Consequently, there would be no control for the production of hydrogen sulfide.

- Since there is no control for excess hydrogen sulfide, there is the potential for altering antimony sulfide to a soluble form. Antimony in excess sulfide concentration forms soluble anionic thio-complexes.

LIME PRECIPITATION

Lime precipitation is the most common method of removing antimony from industrial wastewater. The principle involved in lime precipitation is that metals have some low point in their solubility curve at some alkaline pH value. Simple equilibrium calculations for metal hydroxides and oxides have few meaningful examples in the real world. The reasons for the unpredictability include the fact that most metal hydroxides or hydrous oxides are amphoteric and dissolve at some alkaline pH. It is impossible to obtain the optimum pH for precipitation of metals in a complex mixture.

The aqueous chemistry of antimony ions cannot be well defined. If antimony behaves similarly to other highly charged trace elements, (i.e., bismuth) it will undergo consecutive proton transfers. Anionic colloidal hydroxopolymers will form with increasing pH and eventually precipitates will form. Consequently, antimony trioxide solubility does not control the solubility of antimony in natural waters. Coagulation is usually effected by metal ion hydrolysis; little information is available on the formation of antimony hydroxides. The kinetics of the formation of antimony precipitates is not available. While the establishment of hydrolysis equilibria is generally very fast when hydrolysis species are simple, this is not the case for antimony, where progressive condensation and hydroxylation lead to multimeric soluble intermediates and finally to insoluble precipitates. The kinetics of hydroxoprecipitation need to be defined for antimony if lime precipitation is a desired treatment method. It is conceivable that under proper conditions lime precipitation could reduce antimony concentration below the solubility limit for antimony trioxide. It would be almost impossible, however, to consistently obtain these ideal conditions in complex wastewaters from mines.

Hannah et al. (13) investigated lime precipitation for treatment of antimony present at initial concentrations of 0.6 mg/l. At pH 11.5, removal efficiency was 28 percent. It is likely that hydrolysis had proceeded to the extent that the soluble hydroxo-polymers of SbO^{+} were largely present but hydrolysis was extensive enough that the hydrolyzed precipitate had begun to form.

The complex hydrolysis reactions of antimony are complicated by the presence of other metals in the mine wastewater. Furthermore, any antimony present as the trisulfide can be solubilized by the alkaline pH (13).

Since this study is concerned only with treatment technologies capable of reducing residual antimony levels to less than 0.5 mg/l, lime precipitation is not recommended and will not be discussed further in this section.

Two other treatment technology areas not covered extensively in this section are plant-specific technologies and technologies which are primarily geared toward water recovery. Plant-specific technologies include zero discharge, recycle, reuse, and solar evaporation options which may be applicable for specific locations and circumstances, but are not generally usable. Technologies which have water recovery as their primary purpose include distillation, freeze drying, reverse osmosis, and electrodialysis. These technologies recover water but usually leave a concentrated solution which requires further treatment or disposal.

ION EXCHANGE

Process Discussion and Process Variables

Ion exchange is an attractive method for removal of small amounts of impurities from dilute wastewater. Important industrial applications for metal ion removal and recovery include rare earth separation, copper and zinc recovery in rayon production, and removal of metals such as gold, copper, nickel, zinc, and chromium from plating rinse waters.

State of the Art

Aside from the conventional anionic or cationic exchange columns, there are several new developments in ion exchange which have potential application for trace element removal. One possibility is chelating resins. The formation of metal chelates with the appropriate resin makes possible the removal of metal ions from solution even in the presence of high concentrations of non-complexing ions.

Chelating resins have a marked selectivity for metals capable of forming coordination complexes; antimony falls into this category. At present, however, chelating resins are more costly and the kinetics of adsorption is significantly slower than with conventional exchange resins (Personal communication: Kenneth C. Jones, Mining Chemicals Group, DOW Chemical Co.). This application should be investigated only where conventional resins fail to achieve the desired treatment level.

Another development in the area of ion exchange utilized by metallurgical industries is liquid ion exchange. This process, which has been adopted successfully by the uranium and copper industries (17), has the potential for recovering metals from industrial wastes.

Liquid ion exchangers such as oil-soluble, water-immiscible, alkylsubstituted phosphoric acid (HDPA) are used in ion exchange. For instance, thorium has been extracted from an acid solution by exchanging the proton of HDPA for positively charged thorium. Stripping the extractant is chemically identical with regenerating ion exchange resin. Similarly, liquid exchangers containing sulfonic, carboxylic, and acidic groups have been developed for cation exchange and exchangers containing amines have been developed for anion exchange (18).

As far as conventional ion exchange is concerned, there are currently several contactors available to house the ion-exchange resin. Continuous countercurrent exchangers have the advantage of greater resin utilization and higher chemical efficiency. The most prominent and promising countercurrent exchangers include:

- Higgins, in which the resin is hydraulically moved as a consolidated resin bed up through a contacting zone. Solution flow is in the direction opposite to resin movement except for brief periods when it is cocurrent. All process steps such as loading, rinsing, and regeneration take place in one unit. The process has broad general application (19).

- Asahi, in which the resin moves as a consolidated resin bed down through the contacting zone in a cyclical manner. Each processing step takes place in a separate vessel. The process is in use in Asahi's cuproammonium rayon plant for recovery of copper from waste spinning solution (19).

- Aconex, which consists of fixed-bed columns which rotate in a merry-go-round arrangement, with the liquid feed distributor above the columns divided into sections to accommodate all process steps (19).

Fixed-bed columns will probably dominate the market for several years. Several variations of fixed-bed exchangers currently exist. For example, the counterflow process is a method in which the regenerant is passed upward against a simultaneous downflow of water that joins the regenerant solution at a collector located at the surface of the resin bed. This provides high regenerant efficiency and generally a high-quality effluent (19).

Applicability to Antimony Removal

Although nearly every known metal has been investigated for its treatability with anionic and cationic exchange, commercial-scale applications are far more limited. Ion exchange has reportedly been used effectively for the removal of antimony from ethylene glycol wastewater in pilot-scale applications but data are not available (Personal communication: Mr. Button, Rohm and Haas). An anion exchange resin is applicable to the removal of antimony with a theoretical exchange capacity reported to be 0.07 g/cm^3 (20). This supports the hypothesis that the prevalent aqueous form of antimony is anionic (due to extensive hydrolysis).

Antimony has been successfully treated with Rohm and Haas Amberlite CG-400, a strong basic chromatograph grade exchange resin (21). Presumably a less costly grade anion exchange column would be used on a commercial scale. Dow Chemical manufactures strong base anionic exchange resins, but data on the effectiveness of these resins for antimony treatment are not available.

Final application of ion exchange to the treatment of complex wastewaters from mines or smelters containing antimony will require case-by-case examination of the wastewater components. Exchange columns specific for antimony are not available. The selectivity of a resin for antimony needs to be determined in the specific complex wastewater. The

presence of interfering substances such as humates will need to be investigated.

Pollution Potential

The major problem with the use of ion exchange is the regenerate waste which is produced. The regenerate brine must be treated, although generally this is more easily accomplished than treating the original waste. A large percentage of the regenerating chemicals pass into the effluent unchanged, reflecting the inefficiency of the process.

STARCH XANTHATE

Process Discussion

A water-insoluble starch xanthate (ISX) offers a unique method for removal and recovery of heavy metals from wastewater. ISX acts as an ion-exchange material removing the heavy metal ions and replacing them with sodium and magnesium. The average capacity is 1.1 to 1.5 meq of metal ion per gram of ISX (22). For use in heavy metal removal, a product containing both sodium xanthate and magnesium xanthate is added to the effluent as a solid or slurry, allowing the pH to rise above 7 for optimum removal (23). Metal removal is instantaneous. For continuous flow streams the aid of a clarifier, centrifuge, or filter should be used to settle the sludge. The sludge is roughly 50 percent solids and can be further increased in solids content to about 90 percent after three hours of settling. Metals can be recovered from the ISX sludge by nitric acid treatment or incineration.

State of the Art

There are currently few commercial applications of ISX for heavy metal removal, although 50 to 55 companies are now investigating the feasibility of its use. A plating company in the Northeast has been using ISX for about three years as a filter precoat to reduce concentrations of copper, nickel, and tin-lead (Personal communication: Mr. A. Bessimer, Extract Systems).

ISX has been evaluated for treatment of copper etching rinse waters. Copper concentrations were lowered from 28 to 54 mg/l to less than 0.1 mg/l using ISX (22). This research was conducted as part of an overall evaluation of wastes treatment from the plating industry. ISX systems have also been designed for copper-dye removal (4.73×10^6 liters) and

copper-lignin removal for a stream containing 100 mg/l of copper at 90.7 m^3/hr (22). ISX has a limited stability in solution and would have to be prepared every few days and then diluted for daily use. It is currently available in solid form from at least one supplier, Allen Bessimer Extract Systems (Personal communication: R.E. Wing, U.S. Department of Agriculture).

Application to Antimony Removal

The effectiveness of starch xanthate in removing antimony from wastewater has been investigated in bench-scale tests: 0.05 g/l of starch xanthate removed 5 mg/l of antimony to roughly 0.01 mg/l (Personal communication: Mr. John Zschiegner, J&J Materials).

The Mogul Corporation performed laboratory investigations on a wastewater stream containing antimony at 5.0 mg/l and a COD of 2000 mg/l (Personal communication: Mr. John Bell, Mogul Corp., Chargrin Falls). Of the four processes shown below, only starch xanthate could effectively reduce antimony to the target 0.5 mg/l:

- Lime precipitation did not produce antimony levels below 1 mg/l.
- Oxidation with chlorine and permanganate had no effect.
- Sulfide precipitation was effective only to 3.5 mg/l.
- Starch xanthate effectively reduced antimony level to 0.5 mg/l.

Further investigation into antimony removal by starch xanthate would be required for commercial application. Little is known about how other trace metals in the complex effluent would effect antimony removal.

Pollution Potential

The ISX method has a very low pollution potential. The ISX-metal sludge dewaters easily up to a 90 percent solids level (22). If metal recovery is warranted, the metals can be released from ISX by treatment with nitric acid, thereby avoiding potential leaching problems. Furthermore, nitric acid treatment allows recovery of the crosslinked starch, although it is neither practical nor economical to reuse the starch. If the sludge is landfilled without metal recovery, leaching potential is expected to be limited, since the metal ions are tightly bound to the ISX (23).

ACTIVATED CARBON

Process Description

Adsorption is a phenomenon long recognized for its value in scavenging and retaining soluble metals even at very low concentrations. While activated carbon adsorption is utilized only to a limited extent by the mining and metals industry, under proper conditions of pH and oxidation certain metals will be adsorbed very strongly.

Lignite-based activated carbons are generally used for trace metal recovery. Lignite-based carbons are effective because of the distribution of pore size and the large volume of pores resulting in a high surface area per unit weight. Probably the most important factor in metallic ion adsorption is the pH. Several applications have shown that adsorption improves with decreasing solubility (24). By maintaining the pH at low solubility, carbon loading can be greatly improved.

Several possible mechanisms exist for heavy metal removal by activated carbon (25):

- Ion Exchange - All commercial activated carbon contains some functional groups containing oxygen on the carbon surface. Since the basic carbon skeleton is graphitic in nature, phenolic, carboxylic, ether, peroxide, lactone, and hydroxyl groups may exist.

  The total number and type will depend upon thermal history and upon the oxidants to which it is exposed. Exchangeable sites act in a manner analogous to ion exchange. Most exchange groups are cationic acceptors, although some anionic acceptors do exist.

- Filtration or Entrapment - Granular beds of activated carbon can act as a very effective filtration device. Strong surface forces surrounding the suspended or colloidal material induce the coagulation of particles clinging to the rough activated carbon surfaces.

- Reduction to Metal or Oxidation to Insoluble Forms - The carbon surface may contain several impurities such as ferrous salts or sulfides which can reduce certain metals to elemental forms. Similarly, in the presence of dissolved oxygen, oxidation of certain trace elements occurs.

- True Adsorption - In true adsorption the dissolved species are attracted to the gross interior surface of the carbon and establish dynamic equilibrium between a concentrated surface layer and a dilute solution in the pore space.

State of the Art

The existence of many surface phenomena responsible for trace metal removal by activated carbon offers several areas of research for potential improvements in the activated carbon process.

One area of current investigation is the development of carbons with specially prepared oxygenated surfaces, which enhance adsorption by reacting with cations to form salts. There are no commercial processes employing such carbons, but several Russian investigators have observed increased carbon activity in the presence of oxidation surfaces (25).

Chelation has been used effectively in activated carbon treatment. Cyanide, EDTA, thiourea, lignins, etc., are under investigation as complexing agents to improve adsorption by activated carbon (25). Another variation of chelation which offers potential for improving trace element removal is referred to as "loaded carbon." Specific chelating and complexing agents are adsorbed onto the carbon, providing specific sites for metal adsorption. Sorption capacity corresponds to the stability of complexes formed by the ions and consequently the carbon can be made more selective. Some of the chelating agents under investigation for removal of certain trace elements are: 8-hydroxyquinoline, citric acid, tartaric acid, salicyladoxime, and dibenzoylmethane (25).

The choice of whether to use powdered or granular activated carbon is generally evaluated on a case-by-case basis. Granular carbon, however, is ordinarily the method of choice for a continuous process. Its overall efficiency for a given operation can be greater than that for powdered carbon because a countercurrent effect is attained in a granular carbon bed.

There are currently several applications of activated carbon treatment in the metals industry which suggest that this technology could be used in treating antimony from mine wastes.

- Carbon has been successfully used in this country and in Canada for removing mercury from mercury cell chlorine/caustic plant wastewater. The carbon has been found to be effective in dilute

solutions and has capacity for the metal in several forms (26).

- Granular activated carbon has been used successfully to recover gold from low-grade ores and tailings (26).

- Granular activated carbon has been used to recover molyoxides from sulfide tailings (26).

Application to Antimony Removal

The results of Sigworth have shown that the optimum pH for antimony removal is 0 to 1 (27). At this pH the degree of loading is 16 percent adsorbed, based on carbon weight. Antimony adsorption has been found to be nearly linear with carbon dosage (Personal communication: Mr. J. Dick, ICI. United States). Table 11 indicates that at the optimum pH, antimony is removed more effectively than most metals and that tin was the only other metal effectively removed in this same pH range. In mining wastewaters where several other trace elements may be present in concentrations high enough to warrant treatment, activated carbon, at ideal conditions for antimony removal, will not remove most trace elements.

TABLE 11. ACTIVATED CARBON ADSORPTION OF SELECTIVE METALS

Metallic ion	Approx. % adsorbed based on carbon wt.	Solution	Best pH range
Copper	2	Nitrate	5-7
Zinc	0.1	Chloride	5-7
Nickel	0.25	Chloride	5-7
Cadmium	0.6	Chloride	5-7
Gold	5-7	Cyanide	11.4
Lead	3-5	Acetate or nitrate	5-7
Antimony	16	Trichloride	0-1
Molybdenum	16	Oxide-pH adjusted HCl or H_2SO_4	2-3
Silver	9-12	Nitrate	5-7
Tin	36-40	Stannous chloride	0.2-2.0
	20-22	Stannic chloride	0.5-2.0

The low pH requirement for antimony removal may make activated carbon an impractical treatment method for the large quantities of wastewater under consideration. The use

of chelates to improve adsorption in a neutral pH range should be investigated. Hannah et al. (13) have illustrated the effectiveness of activated carbon in conjunction with precipitation for treatment of antimony. Activated carbon was found to be moderately effective in polishing the wastewater. Table 12 illustrates percent removal for precipitation followed by activated carbon. Antimony removal was investigated in the presence of five other trace elements. The initial antimony concentration was 0.6 mg/l. Interestingly enough, this treatment was carried out at a neutral pH and suggests that requirements for the low pH may not be necessary to attain the desired effluent level.

TABLE 12. PERCENT REMOVAL WITH REMOVAL TECHNOLOGY COMBINATIONS

Precipitation method	Settling conc.	Filter	Old carbon	New carbon
Lime	21	28*	64*	52*
$FeCl_3$	60	65	71	72
Alum	61	62	75	71

*Values are cumulative. Settling, filtration, and carbon adsorption treatments are consecutive rather than individual.

Antimony was found to accumulate in the upper part of the carbon column, indicating an adsorption or filtration mechanism of removal. Lime precipitation is ineffective at these low concentrations because antimony forms slightly soluble sulfides which dissolve in excess alkali.

The improved effectiveness of the old carbon column in certain cases is probably attributable to the formation of H_2S, which increases the probability of metal precipitation.

Secondary Pollutants

Secondary pollutants from activated carbon are formed during regeneration. Form and extent of pollution depend upon the type of regeneration method used. Thermal regeneration by rotary kiln or multiple hearth furnaces is frequently used in trace element treatment. This method would generate antimony oxides, but these can be recovered.

PEAT MOSS

Process Description

Peat moss is a complex material with lignin and cellulose as major constituents. Such constituents contain polar functional groups, i.e., alcohols, aldehydes, ketonic acids, phenolic hydroxides, and ethers, which are involved in chemical bonding (28). Because of the very polar nature of peat, specific adsorption for dissolved solids is quite high. In addition, peat has a cellular structure and high porosity.

The natural capacity of peat to retain cations is related to the pH of the solution. Above pH 8.5 peat is unstable, and below pH 3.0 most metals will be leached from the peat. Treatment methodology begins by precipitating the metal as a sulfide or hydroxide if the concentration exceeds 1.0 mg/l. The metal sulfide or hydroxide is then circulated over a mat of peat which physically adsorbs the metal hydroxide or sulfide. The remaining metal in the form of an ion in solution is then removed by chemisorption. The mat of peat is a 0.7 to 1.0 percent peat slurry which is pumped to a feeding loop located above a slowly moving screen belt. The screen extracts the peat from the slurry and the through water is recycled to a wetting tank (29).

State of the Art

The peat removal process is accomplished by the patented Hussong/Couplan process. Hussong-Walker-Davis has demonstrated the process on an apparatus with a 75,700 l/day capacity. With a peat mat approximately 2.5 cm thick, the hydraulic capacity can be as high as 17 l/m^2 per hour (28). As a first approximation, results have indicated that for solutions containing less than 10 mg/l total metals, 0.96 to 2.4 kg of peat can purify 1000 liters of wastewater. Tests have also shown that several grades of peat are suitable for the process.

The process is currently used by the Nashua Corporation in Nashua, New Hampshire, to treat a 22,700 l/day effluent from the chrome plating of aluminum computer discs (29).

Applicability to Antimony Removal

Antimony removal has been demonstrated using the 75,700 l/day capacity pilot plant. After adjustment of pH in the range of 8.0 with lime followed by settling, the wastewater level containing 2.5 mg/l dissolved antimony was reduced to 0.9 mg/l. Reduction of other heavy metals present in the

wastewater was in all cases more effective than removal of antimony, as indicated in Table 13.

In wastewaters with high organic content, removal with peat is more effective. This has been borne out in the treatment of dye house effluent, with COD of 1200 mg/l and BOD of 150 mg/l. Antimony was reduced from 30 mg/l to 0.5 mg/l. Antimony in this wastewater was in solution, rather than suspended, and removal involved chemical adsorption and complexing (24).

Secondary Pollutants

Disposal of used peat is accomplished by burning or landfilling. Preliminary leaching studies have indicated that peat can be disposed of in landfills without danger of leaching if the metal has been chemisorbed on peat as an ion.

SODIUM BOROHYDRIDE

Process Description and Process Variables

An article in "Process Engineering," 1975, states that the basic process of sodium borohydrate reduction is similar to normal chemical precipitation. The treatment includes pH adjustment, sodium borohydrate addition for reduction and precipitation and clarification and/or filtration for solids/liquids separation. The treated effluent may require additional polishing with a carbonaceous adsorbent or suitable chelate or exchange resins. The sludge contains elemental metals which may eliminate the need for sludge handling facilities and ultimate disposal problems can possibly be avoided. However, if metals recovery is desirable some sort of metal separation will be necessary (hydro or pyrometallurgy). Sodium borohydride is a water soluble reducing agent which can effectively reduce metals by four possible mechanisms (30).

- Reduction to a Lower Valence State -- This reaction generally involves transition elements and the reaction rate is limited by the rate of dissociation of the borohydride ion.

- Reduction to a Free Element -- This reaction is typical of the heavy transition metals and often leads to the quantitative precipitation of these metals from solution. This reaction generally proceeds to the intermediate formation of a metal hydride or borohydride which is unstable in water and subsequently decomposes to form the free metal.

TABLE 13. TREATMENT OF WASTEWATERS CONTAINING HEAVY METALS

Case no.		Before treatment (mg/l)	After treatment (mg/l)	EPA limits (mg/l)	Treatment
1	Pb	20	0.025	0.05	Adjustment of pH in the range of 8.0 with lime. Settling. Contacting with peat.
	Sb	2.5	0.90		
	Cu	1.0	0.2	0.2	
	Zn	1.5	0.25	0.5	
	Ni	2.5	0.07	1.0	
	pH	1.6	7.1	6-8.5	
2	Cu	250	0.24	0.2	As above.
	Ni	67.5	0.5	1.0	
	Zn	7.5	0.08	0.5	
	pH	2.5	7.2	6-8.5	
3	Cu	26,400	0.24	0.2	As above.
	Ni	5,000	0.5	1.0	
	Zn	10	0.16	0.5	
	pH	0.1	7.2	6-8.5	
4	Cr^6	36,000	<0.04	0.04	Adjustment of pH at 7.0 with lime. Treatment with $FeCl_3$/ Na_2S. Settling contacting with peat.
	pH	1.5	7.0	6-8.5	
5	Cu	5.0	0.25	0.2	Addition of $FeSO_4$ and Na_2S. Settling. Contacting with peat. Further reduction of CN to 0.03 by aeration.
	Zn	4.6	0.10	0.5	
	Fe	1.0	<0.05	0.5	
	Ni	13.5	0.6	1.0	
	CN	36.0	0.7	0.03	
	pH	7.75	8.0	6-8.5	

- Formation of Volatile Hydrides -- This is the principal reaction mechanism for heavy elements of groups IV-A, V-A, and VI-A. Volatile hydride formation is the reaction mechanism which would prevail for the reduction of antimony. The reaction generally requires acid conditions; to avoid the competing side reaction of hydrolysis, sodium borohydride is generally added as alkaline borohydride to an acid solution.

- Formation of Insoluble Borohydrides -- Treating of transition metal salts with borohydrides in basic aqueous media can lead to the formation of insoluble borides. This reaction is not frequently observed, although this may be because the insoluble borohydrides react readily in air.

There are certain advantages to using sodium borohydride for treatment of metals in place of precipitation. Elemental metals could be recovered directly and therefore no bulky precipitates would be generated. Furthermore, sodium borohydride is chemically very efficient. It can provide eight available electrons for reduction. Since one lb (454 g) of sodium borohydride contains 12 moles, 96 equivalent weights could be supplied by one lb (454 g) (31). In practice, of course, presence of other reducible compounds may alter the required borohydride. Metal ratio and 100 percent excess borohydride is recommended to insure complete reduction (31). One very important variable is the pH range. At a pH of less than 8, borohydride consumption increases due to hydrolysis and hydrogen gas is formed, while at a pH higher than 11, the rate of metal reduction decreases (31).

A second important variable is the mixing efficiency. Because sodium borohydride is generally used for treatment of low levels of dissolved metals, efficient mixing with the stream is essential. In continuous processing, it is recommended that sodium borohydride be metered into a waste stream through a mixing tee (31).

State of the Art

The sodium borohydride system has been commercially proven for mercury removal in chlor-alkali plants and mercury processing plants. Soluble inorganic mercury compounds are reduced at pH 9 to metallic mercury by carefully metering the required amount of sodium borohydride directly into

the effluent stream. One gram of $NaBH_4$ successfully reduces 21 grams of mercury (30,31).

Another commercial application which has been realized is the removal of dissolved lead compounds from wastewater and effluents generated in the manufacture of tetra-alkyl-lead. Treatment of these waste streams produces a precipitate which may be separated by filtration or settling (30,31).

A third area of application which proves the effectiveness of the $NaBH_4$ process is the quantitative recovery of silver from photographic fixing solutions by reducing it to the free metal (30).

For each specific application of $NaBH_4$, several variables should be examined, as they influence the final product. These include pH, temperature, redox potential, and the order of addition of acid, base, and $NaBH_4$.

Sodium borohydride is available through the Ventron Corporation as a 12-percent solution of sodium borohydride in caustic soda, and as hydroscopic sodium borohydride powder or pellets (32). The advantage of the solution is that it is of low viscosity, easy to handle, and already basic in nature.

Applicability to Antimony Removal

As has been mentioned, antimony reacts with sodium borohydride to yield the corresponding volatile hydrides. Stibine can be obtained by the dropwise addition of alkaline borohydride solution of antimonite to aqueous acid. Assuming that all four hydrogens of the borohydride ion are available for hydride formation, the equation would be:

$$3BH_4^- + 4H_3SbO_3 + 3H^+ = 3B(OH)_3 + 3H_2O + SbH_3$$

Application of sodium borohydride for antimony removal has been demonstrated in the manufacture of ethylene glycol. Antimony is a contaminant of ethylene glycol and can be removed effectively using sodium borohydride (Personal communication: Mr. Douglas Littlehale, Ventron Corporation). Ventron, however, has not had the same success in treating antimony in wastewater. Although quantitative information is not available, antimony cannot be removed as effectively from wastewater as it can from ethylene glycol using the sodium borohydride process. More research is needed on the feasibility of sodium borohydride for antimony removal.

Secondary Pollutants

There is a potential for the release of hydrogen gas resulting from hydrolysis of aqueous borohydride solution. This problem can be minimized in properly designed systems by venting correctly and assuring the absence of external ignition sources.

SECTION 6

COST AND FEASIBILITY ANALYSIS

SUMMARY

The five antimony removal technologies discussed in Section 5 were analyzed, as described in this section, for overall potential for removing antimony from mining industry wastewaters to the desired minimum levels. Through use of evaluation techniques described later in this section, it has been determined that the two most promising technologies for removing antimony to a level of less than 0.5 mg/l are ion exchange and insoluble starch xanthate. In overall feasibility rating, none of the other technologies approaches these two. The relatively high rating for these two technologies follows from a combination of high technical probability of successful application and fairly low costs as compared with the values for carbon adsorption, sodium borohydride treatment, and peat moss adsorption.

Carbon adsorption and sodium borohydride technologies have rather low ratings due to a combination of fairly high treatment costs and relatively low technical probabilities based on reported questionable performance and/or problems such as pH requirements.

Peat moss adsorption has the highest estimated cost of the five technologies, combined with the lowest technical probability. The low technical probability is based primarily on ambiguous and questionable performance reported in the available literature.

In order to keep ion-exchange and insoluble starch xanthate removal technologies in perspective, however, it should be emphasized that:

- As removal technologies for antimony, both ion exchange and insoluble starch xanthate are still in the research laboratory stage, and only a small amount of work has been done at this level.

- Down to a level of approximately 1.0 mg/l residue antimony concentration, lime precipitation has been widely demonstrated to be the most practical and economical antimony removal technology.

- Both ion exchange and insoluble starch xanthate antimony removal technologies should be considered as polishing operations to remove most of the last mg/l of antimony remaining after other treatment.

- Other antimony removal or control technologies such as zero discharge, recycle, water reuse, process stream segregation, and solar evaporation are often feasible in individual mining wastewater situations. These options should be explored prior to turning to the technologies evaluated in this section.

INFLUENCING PARAMETERS

The parameters or factors that determine the applicability of pollutant removal technologies to wastewater streams are both numerous and interactive. These factors must be considered for analyzing the cost and feasibility of different antimony removal technologies as applied to antimony-containing wastewaters from the mining industry. The following discussion covers the pertinent parameters involved in the removal process. No attempt has been made to address the sludge removal and disposal problem.

The parameters may be divided into three categories:

(1) Wastewater-related

(2) Technology-related

(3) Plant-specific.

Wastewater-Related Parameters

Wastewater-related parameters include the volume of the stream and its composition.

Volume--

The cost of most antimony removal technologies depends heavily on the volume of water to be treated. The above relationship can be expressed as an equation of the form:

$$C = K(V)^x$$

where C = The cost in dollars
K = A constant specific to the technology
V = Volume of wastewater stream
x = An exponent ranging from 0.5 to 1.0, depending on the technology.

In the above equation, for technologies where capital equipment is the major cost component, x usually ranges from 0.6 to 0.8. In cases where material costs (such as for lime or other treatment chemicals) predominate, x usually ranges from 0.8 to 1.0.

The cost-volume relationship makes almost any technically feasible removal technology usable for very small-volumed wastewaters, but narrows the practical selection available as the volume increases.

Composition--

The effects of the composition of the wastewater stream on the feasibility and cost of antimony removal technologies are more complex than the cost-volume relationships. Generally these effects may be related to:

(1) Antimony concentration

(2) Antimony form

(3) Other materials present.

Antimony concentration--Most of the antimony concentrations found in mining industry wastewaters, particularly after lime treatment for removal of other metals, are less than 2 to 3 mg/l. Two counteracting factors are involved at this concentration level. The favorable factor is that a wide range of antimony removal technologies are economically feasible. Adsorptive technologies such as ion exchange and activated carbon treatment, for example, often become more economically practical as the amount of material to be adsorbed decreases. Chemical treatments are also economically feasible because of the small amounts of chemicals required to react with the antimony present. On the other hand, as the antimony concentration decreases, the removal efficiency often decreases as well. As an example, antimony precipitation with chemicals such as lime and sulfide may be very effective in reducing the concentration of antimony from 100 mg/l to 2 to 3 mg/l (97 to 98 percent removal) in a given wastewater, but as the solubility limits of antimony hydroxides and sulfides are approached, such as for a 2 mg/l antimony-containing wastewater, only 0 to 5 percent removal may be achieved. At low concentrations interference from other ions, chelating agents, and complexing chemicals must

be considered, as should precipitation kinetics and adsorptive effects.

Antimony form--Although the physical and chemical form of a pollutant present in wastewater should be identified prior to any removal technology consideration, this is not always the case. Almost all analytical data on antimony in mine wastewater is reported on a "total" basis that includes both suspended and dissolved portions. Particularly in the range of 1 to 2 mg/l metal concentration, the physical form in which the metal exists is all-important in determining the treatment required. Often simple filtration will reduce the "total" metal content from an initial 1 to 2 mg/l level to 0.5 mg/l or less. This reduction indicates that much of the initial "total" metal was in the form of finely divided suspended solids. A second concern is the chemical form of the metal present in the wastewater. In many cases the metal may be present as an insoluble inert component of rock or earth particles. In other cases, it may be present in a relatively soluble and reactive chemical form, or in the form of a complex or chelate.

Other materials--Mining industry wastewaters contain a wide variety of metallic compounds as well as nonmetallic materials. The concentration of antimony is often much lower than that of several other toxic metals which have to be removed. Therefore, any overall treatment processes have to address removal of both antimony and the other toxic metals. In many cases this removal will require a multistage treatment, of which lime precipitation constitutes the first stage.

The presence of other metals and nonmetals in antimony-containing mining industry wastewaters must be taken into account for several reasons, including:

(1) The other metals and nonmetals may interfere with antimony removal performance. Antimony may form a complex or chelate with one or more of the other materials present. Bulky precipitates of other metals may make filtration difficult.

(2) Chemicals used to precipitate antimony may react with and precipitate other metals as well. This will require significantly more of the chemical than is needed for antimony removal alone and will increase the treatment costs accordingly.

Technology Factors

In determining the applicability of technologies for antimony removal from mining industry wastewater, there are a number of factors which must be considered, including:

(1) Pollutant removal level required

(2) State of development

(3) Equipment required

(4) Materials required

(5) Specificity

(6) Sensitivity to interferences.

Pollutant Removal Level Required--

Antimony is removed from mining industry wastewater to the level of 1 to 2 mg/l by means of lime precipitation. It is not possible to achieve lower concentrations with this technology alone. Therefore, if antimony must be removed to the 0.1 to 0.5 mg/l level, lime precipitation is not appropriate. On the other hand, distillation could readily achieve the 0.1 to 0.5 mg/l residual antimony level but would be very expensive. The removal technology must be capable of achieving the desired level at a practical cost.

State of Development--

The state of development is an important factor in selecting applicable antimony removal technology. Technologies that have been known for years and are still laboratory curiosities are probably not practical and, at best, will require extensive effort to move them to demonstration status. Technology demonstrated on the wastewaters of other industries usually has a much better potential for success, but there have been many instances where the transfer from one industry to another has caused unexpected problems.

Equipment Required--

Capital investment cost to install treatment equipment is always a factor to be considered. In addition to the capital costs, however, consideration also should be given to operation and maintenance.

Materials Required--

When chemicals are used as precipitants, adsorbents, or reactants in antimony removal technologies, the costs for these materials often constitute the major expense involved. Moreover, the material costs are often directly proportional to the amount of antimony to be removed.

Specificity--

Some removal technologies are more specific than others with regard to their ability to remove only the desired pollutant. Fortunately, most antimony removal technologies are not very specific and will remove other metals as well.

Sensitivity To Interferences--

One of the major difficulties with many pollutant removal technologies is that some component of the wastewater interferes with the desired removal performance. Distillations, reverse osmosis operations, adsorptions, and other removal technologies often require major wastewater pretreatment. Failure to provide this pretreatment leads to plugging, corrosion, or fouling of the equipment. Other materials present may also change solubility, reactivity, and settling characteristics.

Plant-Specific Factors

In addition to the more general wastewater and technology factors, there are others of a more site- or plant-specific nature. These factors depend on special circumstances such as:

(1) The process used

(2) Value of the product produced

(3) Waste recovery value

(4) Reuse capabilities

(5) Geographic location and topography.

The Process Used--

Different processes may be used to produce the same end product. The wastewater from each process is usually specific, differing significantly in both volume and composition from those of other processes.

Value of the Product--

In order to estimate the economic impact of installing pollutant removal technology on a plant or industrial subcategory, calculations are usually made of the costs per unit of product and/or costs as a percentage of selling price. A cost increase of $1 per metric ton of produced silver is likely to have a significantly different impact than would a similar increase for a metric ton of sand or gravel.

Waste Recovery Value--

In some instances, the wastewater to be treated contains valuable materials which can be recovered and sold or reused. Prime examples are wastewaters containing gold or silver. The value of the recovered gold or silver can underwrite the development and use of complex technology and expensive treatment systems that would not otherwise be practical.

Reuse Capabilities--

Reuse of components of the wastewater stream can be applied either to the water or to the materials recovered from it. As the availability of water decreases and its price increases, more and more attention is being given to its recycle and reuse. Recycle and reuse not only make more complex treatment technology economically feasible, but also constitute one of the more desirable forms of pollutant control in that there is no discharge from the plant environs.

Geographic Location and Topography--

Plant-specific factors such as geographical location and local topography may have pronounced effects on the cost and feasibility of wastewater treatment technology. For example, in dry climates solar evaporation may be feasible. It is not practical in areas with heavy rainfall. In other cases, plants may be located on small urban plots with no room for settling ponds or other large-area treatment facilities. In hilly or mountainous terrain wastewater may be dammed in valleys and stored, percolated, or evaporated at a fraction of the treatment costs for flat-land installations.

FEASIBILITY METHODOLOGIES

The parameters influencing cost and feasibility of removing antimony from wastewater need to be considered in a systematic, objective fashion.

Feasibility Parameters

Feasibility of antimony removal technology first depends on whether the desired removal level can be reached. For purposes of this study, the inherently achievable level of residual antimony must be less than 0.5 mg/l. Unfortunately, for most technologies, information on antimony removal at this level is usually not available. Therefore, when there is a reasonable possibility that a technology will remove antimony to the 0.1 to 0.5 mg/l level, this technology has been included for consideration.

The second feasibility concern is technical applicability. Applicability includes such factors as consideration of the physical and chemical form of the antimony present, the state of development of the removal technology, industry demonstration, sensitivity to interference, space requirements, availability of equipment and materials, and geographical location. A simple example of inapplicable technology would be the use of filtration equipment to remove dissolved antimony. On the other hand, filtration could be a perfectly applicable technology to remove suspended antimony-containing particles. For purposes of this study, only dissolved antimony removal technology is considered.

The third feasibility concern is economic impact - the influence that the given antimony removal technology will have on the profitability and viability of the mining operation. No attempt is made in this study to estimate the profitability of the mining operations or the influence on this profitability of installing and operating antimony removal technology. Rather, the antimony removal costs are presented in the form of percent of sale values of the mined product(s). For example, if the total annual antimony removal technology cost is $10,000 and the total value of the mined and recovered products is $1,000,000 per year, then the cost would be one percent of product value.

Calculating antimony removal technology cost is not a simple matter. For accurate estimates, each mining operation needs to be considered individually. For rough estimates, however, assumptions may be made which will simplify these calculations. Factors which have significant influence on the costs of antimony removal technologies include:

(1) Research and development costs

(2) Required capital equipment and auxiliary services

(3) Operating materials and labor.

Feasibility Index

The feasibility index developed by Hittman for use in this study is composed of two factors: the probability of successful technology development and the cost impact. This index was used in an attempt to eliminate bias and provide a method of analysis.

The cost impact estimation used for this study has been discussed previously. The probability of successful

technology development is composed of four factors as defined below:

$$P = (L)\ (A)\ (S)\ (R)$$

where P = The probability of successful technical development

L = The probability of achieving the desired removal level, based on theoretical parameters such as inherent solubility

A = Availability of equipment and materials, expressed as a probability between 1.0 and 0

S = The sensitivity of the technology to interferences from wastewater constituents other than antimony, expressed as a probability, with 1.0 representing no interference and 0 representing interference so serious as to make the technology useless

R = The probability of successful research and development efforts overcoming existing problems

The values of L, A, S, and R given for the various antimony removal technologies evaluated later in this section were arrived at by consensus of the two members of the team preparing this report who are most familiar with the available data on antimony removal from water media.

Using the above probability of successful technical development together with the cost impact, the feasibility index is defined as:

$$F = \frac{P}{C}$$

where: F = The feasibility index

C = The cost impact expressed as cost percentage of product value.

The feasibility index defined above can be used to provide a rough comparison of the applicability of given technologies for antimony removal and may also be used with increased precision as additional information is obtained through laboratory, pilot plant, and other applied technology evaluation techniques.

TECHNOLOGY ANALYSES

In order to assess the technical and economic feasibility of antimony removal technologies, it is necessary to establish some basis for technology requirements and cost estimating. Therefore, the following values have been selected for use in all calculations:

Parameter	Value
Wastewater volume	3,785 m^3/day
Mine product value	$10,000,000/yr
Wastewater composition	
Total suspended solids	20 mg/l
Dissolved antimony	3 mg/l
Total dissolved heavy metals	10 mg/l

Although the chosen values for the above parameters do not represent the actual values at any given mine, they can be used for feasibility calculations, particularly for comparison purposes. Using the above parameter values, feasibility indices have been determined for the five potentially usable antimony removal technologies discussed in Section 5.

With the exception of the values for peat moss adsorption technology, which were taken from a published article, all capital costs for treatment equipment installations have been estimated with the additive modular approach, using cost-capacity curves as described in Reference 33. Unless otherwise stated, operating costs were either taken from Reference 33 or estimated using procedures described in Reference 34. Both capital costs and operating costs should be considered order-of-magnitude numbers, with an accuracy of $\pm$ 50 percent.

Ion Exchange Technology

Ion-exchange resins have been used to remove antimony from water and water-ethylene glycol mixtures in laboratory and pilot plant experiments. There is no information on the removal levels achieved.

Technical Probability--

The technical probability index for antimony removal technologies and the method used to arrive at the individual probability values were described in the preceding section. The technical probability index was defined as P=(L)(A)(S)(R). Values of L, A, S, and R for ion-exchange removal of antimony are estimated as:

$$L = 0.8 \qquad S = 0.5$$
$$A = 0.9 \qquad R = 0.7$$

Using these probability values:

$$P = 0.8 \times 0.9 \times 0.5 \times 0.7 = 0.25.$$

Cost Index--

The estimated installed capital costs for a 3,785 m^3/day continuous countercurrent ion-exchange facility are approximately \$150,000 (1972 base) (33). Adjusting this value to July 1978 prices using the Chemical Engineering Plant Cost Index,

$$1978 \text{ Cost} = \$150,000 \times \frac{217}{137} = \$237,600.$$

Estimated operating cost for 10 mg/l removal of antimony and other heavy metals is approximately \$.026/m^3 or \$36,000 per year.

Amortizing the capital costs of the facilities over a 10-year life at 10 percent interest rate,

$$\text{Annual Capital Cost} = \$237,600 \times .1627 = \$38,660.$$

The total annual cost, therefore, for both capital amortization and operation is \$74,680. Dividing this by the product value of \$10,000,000 per year gives:

$$\text{Cost index} = \frac{\$74,680}{\$10,000,000} \times 100 = 0.75.$$

Feasibility Index--

The feasibility index for ion-exchange removal of antimony from mining wastewater is:

$$F = \frac{P}{C} = \frac{0.25}{0.75} = 0.33.$$

Activated Carbon Adsorption

Activated carbon is reported to remove antimony from water in the laboratory. According to one source, the recommended pH for removal is approximately 1, which requires that significant quantities of acid be added to the wastewater prior to removal (24). This cost has not been included in determining the cost index, since others have not reported this requirement (13).

Technical Probability--

Values of L, A, S, and R and the resulting technical probability index are given below:

L = .5

A = .9

S = .7

R = .5

P = .5 x .9 x .7 x .5 = 0.16.

Cost Index--

Estimated installed capital cost for a 3,785 m^3/day facility is $700,000 (1973 base) (33). Adjusting this value to July 1978 prices using the Chemical Engineering Plant Cost Index,

$$1978 \text{ cost} = \$600,000 \times \frac{217}{145} = \$1,050,000.$$

Taking estimated operating costs for 10 mg/l removal of antimony and other heavy metals from Reference 33 and adjusting them for increased energy and labor costs from 1974 gives approximately $\$0.026/m^3$ or $36,000 per year.

Amortizing the capital costs of the facilities over a 10-year life at 10 percent interest rate,

Annual capital cost = $1,050,000 x .1627 = $170,835.

The total annual cost, therefore, for both capital amortization and operation is $206,835. Dividing this total by the product value of $10,000,000 per year gives

$$\text{Cost index} = \frac{\$206,835}{\$10,000,000} \times 100 = 2.07.$$

Feasibility Index--

The feasibility index for carbon adsorption removal of antimony from mining wastewaters is:

$$F = \frac{P}{C} = \frac{0.16}{2.07} = .08$$

Insoluble Starch Xanthate

The use of insoluble starch xanthate to reduce antimony concentration below 0.5 mg/l has been reported from two sources (Personal communications: Mr. John Bell, Mogul Corp., and Mr. John Zschiegner, J&J Materials). Both sources are based on actual laboratory experiments designed for antimony removal.

Technical Probability--

The values of L,A,S, and R for insoluble starch xanthate removal of antimony are estimated as:

L = .9
A = .9
S = .8
R = .7
P = .9 x .9 x .8 x .7 = .45.

Cost Index--

The major capital equipment items needed for use of insoluble starch xanthate treatment of 3,785 m^3/day of wastewater are:

(1) ISX feed system
(2) Reaction vessel
(3) Clarifier
(4) Centrifuge or filter.

Installed capital costs (1973 base) (33) are:

ISX feed system	$ 30,000
Reaction vessel	25,000
Clarifier	85,000
Centrifuge or filter	40,000
TOTAL	$180,000

Converting this cost to July 1978 dollars,

$$1978 \text{ cost} = \$180,000 \times \frac{217}{145} = \$269,400.$$

The annual amortized cost, taken as 10-year life and 10 percent cost of money, is $2,691,400 x .1627 or $43,830.

With the exception of the chemical cost for the ISX, operating costs for the above equipment should be similar to those for other water treatment systems using chemical feeds, reactors, clarifiers, and filters or centrifuges.

Estimated operating costs are (34):

Operating Costs (Excluding Chemicals)

Operating labor and supervision at 4% of capital costs	$10,776
Maintenance, labor and materials at 3% of capital costs	8,082
Analytical services at 1% of capital costs	2,694
Utilities at 3% of capital costs	8,082
General overhead at 2% of capital costs	5,388
Insurance and taxes at 3% of capital costs	8,082
TOTAL	$43,104

Chemicals

The major chemical expense is for ISX. Taking a manufacturer-recommended dosage of 50 mg/l for removing 5 mg/l of antimony to a level of 0.01 mg/l (reported laboratory performance of antimony removal by Mr. John Zschiegner, J&J Materials) as the basis for chemical usage gives:

$$\text{ISX required} = \frac{0.5 \text{ gm}}{\text{liter}} \times \frac{3{,}785{,}000 \text{ liters}}{\text{day}} \times 365 \frac{\text{days}}{\text{yr}}$$

$$= 68{,}985{,}000 \frac{\text{gm}}{\text{yr}} \text{ or } 68{,}985 \text{ kg/yr}$$

ISX cost/yr = $68,985 x 0.77* = $53,100.

The total annual cost of ISX removal of antimony is estimated as $96,200 + $43,800 or $140,000. Dividing this total by the product value of $10,000,000 per year gives:

$$\text{Cost Index} = \frac{\$140,000}{\$10,000,000} \times 100 = 1.40.$$

Although the cost of $0.77 per kg for ISX has been used in the preceding calculations, with the justification that such a large usage would warrant preparation in the plant, ISX is commercially available at $17.60 per kg. The decision for making or buying would have to be made on the basis of cost efficiency.

Feasibility Index--

The feasibility index for insoluble starch xanthate removal of antimony from mining wastewater is:

$$F = \frac{P}{C} = \frac{.45}{1.40} = 0.32.$$

Peat Moss Adsorption

Various natural organic materials such as chitin, peat moss, and other humic substances have been used to adsorb heavy metals dissolved in wastewater. Peat moss adsorption systems have been developed on pilot-plant and commercial scales, and are discussed in detail in Section 5. Only sketchy and somewhat contradictory information has been reported on the performance of these systems for antimony removal.

Technical Probability--

Values of L,A,S, and R and the resulting technical probability index are given below:

L = 0.3
A = 1.0
S = 0.6
R = 0.3
P = 0.3 x 1.0 x 0.6 x 0.3 = 0.05.

**ISX cost/kg, based on user making own ISX (cost supplied by Dr. R.E. Wing, U.S. Agricultural Research Laboratories). Therefore, total annual operating cost is estimated at $43,100 + $53,100 or $96,200.*

Cost Index--

According to Reference 29 the installation costs of a peat moss adsorption system for treating 3,785 m3/day of wastewater are $600,000 (1974 base). Adjusting this to a 1978 cost basis using the Chemical Engineering Plant Cost Index, gives:

$$1978 \text{ cost} = \$600,000 \times \frac{217}{165} = \$789,000.$$

Amortizing this cost over a 10-year period at an interest rate of 10 percent gives:

$$\text{Annual Capital Costs} = \$789,000 \times .1627$$

$$= \$128,370.$$

Operating costs for a peat moss system may be estimated using Reference 34 for calculating operating costs exclusive of peat moss and adding the peat moss costs to this value.

Operating Costs (Excluding Peat Moss)

Operating labor and supervision at 4% of capital costs	$ 31,560
Maintenance, labor, and materials at 3% of capital costs	23,670
Analytical services at 1% of capital costs	7,890
Utilities at 3% of capital costs	23,670
General overhead at 2% of capital costs	15,780
Insurance and taxes at 3% of capital costs	23,670
TOTAL	$126,240

Peat moss requirements are roughly estimated at 1.2 kg/1,000 liters or 4.5 metric tons per day (4). At a delivered price of $50 per metric ton, the annual costs for peat moss are:

$$\text{Peat moss costs} = 4.5 \frac{\text{kkg}}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} \times \frac{\$50}{\text{kkg}}$$

$$= \$82,125.$$

Therefore the total annual operating costs are $82,125 + $126,240 or $208,365.

The total annual cost of peat moss removal of antimony is estimated as $208,365 + $126,240 or $334,605.

Dividing the above total by the product values of $10,000,000 per year gives:

$$\text{Cost Index} = \frac{\$334,605}{\$10,000,000} \times 100 = 3.35.$$

Feasibility Index--

The feasibility index for peat moss removal of antimony from mining wastewaters is:

$$F = \frac{P}{C} = \frac{0.05}{3.35} = 0.01.$$

Sodium Borohydride Precipitation

Sodium borohydride has been used to remove dissolved heavy metals such as mercury from industrial wastewaters, achieving residual metal levels of less than 0.1 mg/l (Personal communication: Mr. D. Littlehale, Ventron Corporation). Experimental results reducing antimony levels from 1,000 mg/l to less than 2 mg/l have been achieved in glycol-water mixtures (Personal communication: Mr. M. Cook, Ventron Corporation). It is also believed that significantly lower residual concentrations should be achievable, particularly when starting with more dilute concentrations of antimony ion (Personal communication: Cook).

Technical Probability--

The values of L,A,S, and R for sodium borohydride removal of antimony are estimated as:

L = 0.6
A = 1.0
S = 0.6
R = 0.5
P = 0.6 x 1.0 x 0.6 x 0.5 = 0.18.

Cost Index--

Removal of dissolved antimony from wastewaters with sodium borohydride requires a chemical storage and feed system, reaction and decanting vessels, and polish filtration to remove residual suspended antimony particles.

The estimated capital costs for a 3,785 m3/day wastewater treatment system are shown below (33,35):

Equipment	Installed Costs (1973 base)
Storage and feed system	$ 30,000
Reaction vessel	25,000
Decanting vessel	25,000
Sand filter system	100,000
Total	$180,000

Converting this cost to July 1978 dollars gives:

$$1978 \text{ cost} = \$180,000 \times \frac{217}{145} = \$269,400.$$

The annual amortized cost, taken for 10-year equipment life and 10 percent cost of money, is $269,400 x 0.1627 or $43,830.

With the exception of the cost for sodium borohydride, operating costs for the above equipment should be similar to those for other water treatment systems using chemical feed systems, reactors, settling vessels, and filters. Therefore operating costs may be estimated from a combination of operating costs exclusive of chemical costs and sodium borohydride costs.

Operating costs excluding sodium borohydride are similar to those previously calculated for the ISX system, or $43,104.

Sodium borohydride costs, based on values supplied by personal communication with Mr. Michael Cook of the Ventron Corporation, follow.

Basis for calculation:

(1) 3 moles of sodium borohydride react with 8 moles of Sb (3).

(2) Four times excess will be required.

(3) A total dissolved heavy metal content equivalent to 10 mg/l of Sb is present in the wastewater (3).

$$\text{Sodium borohydride} = \frac{1 \text{ gr } NaBH_4}{8.58 \text{ g Sb(3)}} \times 4 \times \frac{10 \text{ g Sb(3)}}{m^3}$$

$$\times 3{,}785 \text{ m}^3\text{/day} \times 365 \text{ days/yr}$$

$$\times 1 \text{ kg}/1{,}000 \text{ g}$$

$$= 6{,}440 \text{ kg/yr},$$

Sodium borohydride cost = 6,440 kg/yr x \$33/kg = \$212,920.

Total annual operating cost = \$212,920 + \$43,100

= \$256,000.

Adding the amortized annual capital equipment costs to the annual operating costs gives a total operating cost of \$256,000 + \$43,830 or \$299,830.

Dividing the total annual cost by the product value of \$10,000,000 per year gives:

$$\text{Cost Index} = \frac{\$299{,}830}{\$10{,}000{,}000} \times 100 = 3.0.$$

Feasibility Index--

The feasibility index for sodium borohydride removal of antimony from mining wastewater is:

$$F = \frac{P}{C} = \frac{0.18}{3.0} = 0.06.$$

Discussion of Values

The feasibility, cost, technical probability indices and the L, A, S, and R components of the probability indices for the five antimony removal technologies analyzed in this section are summarized in Table 14, along with those for a sixth removal technology, distillation.

TABLE 14. SUMMARY OF PROCESS APPLICABILITY ESTIMATES FOR ANTIMONY REMOVAL

Technology	F	C	P	L	A	S	R
Ion exchange	0.33	0.75	0.25	0.8	0.9	0.5	0.7
Insoluble starch xanthate	0.32	1.40	0.45	0.9	0.9	0.8	0.7
Carbon adsorption	0.08	2.07	0.16	0.5	0.9	0.7	0.5
Sodium borohydride	0.06	3.0	0.18	0.6	1.0	0.6	0.3
Peat moss adsorption	0.01	3.35	0.05	0.3	1.0	0.6	0.3
Distillation	0.05	13.81*	0.64	1.0	1.0	0.8	0.8

*Calculated from a cost estimate of $1/m3 of wastewater distilled.

$$P = (L)(A)(S)(R)$$

where:

P = The probability of successful technical development

L = The probability of achieving the desired receival level, based on theoretical parameters such as inherent solubility

A = Availability of equipment and materials, expressed as a probability between 1.0 and 0

S = The sensitivity of the technology to interferences from wastewater constituents other than antimony, expressed as a probability, with 1.0 representing no interference and 0 representing interference so deviant as to make the technology useless.

R = The possibility of successful research and development efforts overcoming existing problems.

$$F = \frac{P}{C}$$

F = The feasibility index

C = The cost impact expressed as cost percentage of product value.

Distillation has been included to illustrate the interactions that make the feasibility index a significant overall rating mechanism. Distillation's high values of 1.0 for L and A indicate that theoretically distillation can remove antimony to less than 0.5 mg/l and that equipment exists to carry out such distillations. The 0.8 probability ratings for S and R indicate that although interferences and R&D problems can most likely be overcome, some significant problems exist with pretreatment, corrosion, fouling, and handling of high solids residues. The technical probability index, calculated from L, A, S, and R values, is still very high compared to those for the other five technologies. Estimated cost values for distillation, on the other hand, are roughly ten times those for ion exchange and insoluble starch xanthate removal technologies. In overall feasibility, therefore, distillation rates relatively low as an antimony removal technology for mining industry wastewater.

The overall feasibility index values indicate that ion exchange and insoluble starch xanthate technologies have a definitely higher probability of successful application for antimony removal than any of the other four. Carbon adsorption, sodium borohydride treatment, and distillation have only scant probability of successful application and peat moss adsorption falls at the bottom of the probability rating.

REFERENCES

1. U.S. Environmental Protection Agency. Literature Study of Selected Potential Environmental Contaminants. Antimony and its Compounds. EPA-560/2-76-002, February 1976.

2. Ralph Stone and Co., Inc. Treatment Effectiveness for the Removal of Selected Contaminants from Drinking Water. Prepared for the U.S. Environmental Protection Agency, March 1975.

3. U.S. Environmental Protection Agency. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. EPA 440/1-75/061, October 1975.

4. Leslie, M.E., "Peat: New Medium for Treating Dye House Effluent." American Dyestuff Reporter, August 1974, pp. 15-18.

5. R.K. Guthrie and D.S. Sherry. "Pollutant Removal from Coal-Ash Basin Effluent." Water Resources Bulletin, Vol. 12, No. 5, pp. 889-903.

6. M.L. Hemming. "Effluent Treatment in the Paint and Surface Coating Manufacturing Industry." Paint Manufacture, June 1975, pp. 8-29.

7. Roy E. Williams, et al. The Role of Mine Tailings Ponds in Reducing the Discharge of Heavy Metal Ions to the Environment. Moscow: Idaho Bureau of Mines and Geology, 1973.

8. Calspan. Chemical Analysis Data Supplement to the Addendum to Development Document for Effluent Limitations Guidelines and Standards of Performance for the Ore Mining and Dressing Industry. Prepared for the U.S. Environmental Protection Agency, May 1978.

9. R.S. Ottinger, et al. Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Wastes, Vol. 12, U.S. Environmental Protection Agency 670/2-73-0531, August 1973.

10. U.S. Environmental Protection Agency. Draft and New Data for the Development of Effluent Limitations Guidelines for the Miscellaneous Nonferrous Metals Segment of Nonferrous Metals. EPA-440/1-78/067, January 1978.

11. Sunshine Mining Company. National Pollutant Discharge Elimination System: Discharge Monitoring Reports, Kellogg, Idaho, Sunshine Mining Company, 1978.

12. STORET Retrieval Data. USEPA Region X. Pacific Northwest, Spokane River Basin, 1119CO50.

13. Hannah, A., M. Jelus, J.M. Cohen. "Removal of Uncommon Trace Metals by Physical and Chemical Treatment Processes." Journal of the Water Pollution Control Federation, November 1977, pp. 2297-2309.

14. Cotton, F.A. and G. Wilkinson. Advanced Inorganic Chemistry. Interscience Publisher, 1966, pp. 486-518.

15. Stumm, W. and J.J. Morgan. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, New York: Wiley-Interscience, 1970, pp. 238-299.

16. Permutit Company. Proceedings of Seminar on Metal Wastes Treatment Featuring the Sulfex Process. Paramus: Permutit Company, 1975.

17. Dean, J.G., F.L. Bosqui and K.H. Lanouette. "Removing Heavy Metals from Wastewater." Environmental Science and Technology, Vol. 6, No. 6 (1972), pp. 518-522.

18. Calmon, C. "Trace Heavy Metals in Water: Removal Processes by Ion-Exchange." In: Traces of Heavy Metals in Water Removal Processes and Monitoring, U.S. Environmental Protection Agency, EPA-902/9-74-001, 1973, pp. 7-42.

19. Wheaton, R.M. and A.H. Seamster. A Basic Reference on Ion Exchange. The Dow Chemical Company, 1977, pp. 871-899.

20. Kunin, R. "Ion Exchange for the Metal Products Finisher." Rohm and Haas, Reprinted from Products Finishing, 1969, p. 24.

21. U.S. Environmental Protection Agency. Treatment Effectiveness for the Removal of Selected Contaminants from Drinking Water. EPA-68-01-2692. Prepared by Ralph Stone and Company, Inc., 1975, p. III-15.

22. Wing, R.E. "Processes for Heavy Metal Removal from Plating Wastewaters." Presented at: American Society of Electroplated Plastics, 10th Annual Meeting, San Diego, November 16-19, 1977.

23. U.S. Department of Agriculture. Insoluble Starch Xanthate: Preparation and Use in Heavy Metal Removal. CA-NRRC41 (Rev. 2). Peoria: Northern Region Research Center, June 1976, pp. 1-7.

24. ICI United States, Inc. Activated Carbon in the Metals Industry. Wilmington: Specialty Chemicals Division, 1976, pp. 1-8.

25. Smith, S.B. "Trace Metals Removal by Activated Carbon." In: Traces of Heavy Metals in Water Removal Processes and Monitoring. EPA-902/9-74-001. New York's U.S. Environmental Protection Agency, 1973, pp. 55-70.

26. ICI United States, Inc. Chemicals for the Metals Treating Industry. Wilmington: ICI-Specialty Chemicals Division, 1977.

27. Sigworth, E.A. "Potentialities of Activated Carbon in the Metallurgical Field." In: AIME Proceedings, New York: American Institute of Mining, Metallurgical, and Petroleum Engineers, 1962.

28. Coupal, B. and J. Lalancette. The Treatment of Waste Waters with Peat Moss. Cornwells Heights: Hussong-Walker-Davis Company, 1975.

29. Krewson, W.G. "Heavy Metal Removal with Sphagnum Peat." Presented at American Institute of Chemical Engineers Symposium, Atlantic City, 1976.

30. Ventron Corporation, Inorganic Reductions with Sodium Borohydride: Principles and Practices. Beverly: Ventron Chemicals Division, 1974.

31. Ventron Corporation. Heavy Metal Recovery with Sodium Borohydride. Beverly: Ventron Chemicals Division, Technical Bulletin #47-A. n.d.

32. Ventron Corporation, A Stabilized Water Soluble Solution of 12 Percent Sodium Borohydride in Caustic Soda. Beverly: Ventron Corporation. n.d.

33. U.S. Environmental Protection Agency, Development Document for Proposed Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category, Supplement A, EPA-400/1-75/037, Group I, Phase II, Supplement A, Washington, DC, 1975.

34. Parker, C.L. and C.V. Fong. "Estimation of Operating Costs for Industrial Wastewater Treatment Facilities." American Association of Cost Engineers Bulletin, December 1976, pp. 207-211.

35. Parker, C.L. and C.V. Fong. "Use of Sand Filters In The Ceramics Industry." Filtration Engineering, Sept./Oct. 1975, pp. 6-7.